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# **Development of a remediation strategy for surface soils contaminated with energetic materials by thermal processes**

*Phases 1, 2 and 3*

*Isabelle Poulin  
Gaston Nadeau  
Annie Gagnon  
DRDC Valcartier*

**Defence R&D Canada – Valcartier**

Technical Report

DRDC Valcartier TR 2009-150

November 2009

Canada



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## Abstract

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As a result of military training, many ranges and training areas are contaminated with energetic materials (EMs). In Canada, for many sites characterized, more than 80 % of the overall contamination by EMs was found in the first 10 cm of the surface soil for propellant residues at the firing positions. Military personnel can be exposed to these compounds which may eventually be transported to surface and groundwater. At this moment, there is no official protocol for routinely removing propellant residues from surface soils. Various remediation strategies are currently being studied (phytoremediation, fire ecology, etc.) in order to address the problem of surface soils contamination by EMs. This report presents the work carried out to evaluate up to which extent the combustion of selected fuels (liquids and gels) could be used as a remediation method for the thermal decomposition of propellants in surface soils. In Phase 1, preliminary tests were carried out to quickly evaluate the potential of fuel combustion over soil as a remediation procedure. In Phase 2, temperature propagation in sand was determined during burnings. In Phase 3, contaminated soil taken from the firing position of an anti-tank range was monitored for nitroglycerine before and after the combustion of a top layer of selected fuels. The results showed that a gelled ethanol fuel is promising for the remediation of contaminated soils by energetic materials.

## Résumé

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En raison des exercices d'entraînement militaire, plusieurs sites sont contaminés par des matériaux énergétiques. Au Canada, dans plusieurs pas de tir contaminés par les résidus de poudres propulsives, plus de 80 % de la contamination totale se trouve dans les premiers 10 cm de sol. Le personnel militaire peut être exposé à ces composés qui peuvent aussi être transportés dans l'eau de surface et souterraine. Actuellement, il n'y a pas de protocole officiel pour retirer périodiquement les résidus de poudres propulsives des sols de surface. Plusieurs stratégies de restauration sont présentement à l'étude (phytoremédiation, écologie du feu, etc.) dans le but d'examiner le problème de la contamination des sols de surface par les matériaux énergétiques. Ce rapport présente les travaux réalisés pour évaluer à quel point la combustion de carburants (liquides et gels) pourrait être utilisée comme méthode de restauration pour effectuer la décomposition thermique des résidus de poudres propulsives dans les sols de surface. Durant la Phase 1, des tests préliminaires ont été réalisés pour évaluer rapidement le potentiel du brûlage d'un carburant sur un sol contaminé comme procédure de restauration. Durant la Phase 2, des mesures de propagation de la température dans le sable ont été prises durant des brûlages. Durant la Phase 3, du sol contaminé pris sur un pas de tir d'un site anti-char a été analysé pour mesurer la nitroglycérine avant et après la combustion d'une couche de combustibles sélectionnés. Les résultats montrent qu'un gel à base d'éthanol est très prometteur pour la restauration des sols contaminés par les matériaux énergétiques.

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## Executive summary

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### **Development of a remediation strategy for surface soils contaminated with energetic materials by thermal processes: Phases 1, 2 and 3**

**Isabelle Poulin; Gaston Nadeau, Annie Gagnon; DRDC Valcartier TR 2009-150; Defence R&D Canada – Valcartier; November 2009.**

**Introduction or background:** To ensure a high degree of preparedness of military troops for any potential mission, training with live weapons is an important part of the military activities. As a result of this training, many ranges and training areas are contaminated with energetic materials (EMs). Propellant residues accumulate at firing positions and projectiles filling may be spread near the targets, for example when an unexploded ordnance (UXO) is fractured after being hit by shrapnel or other fragments.

For most of the Canadian ranges where environmental characterization has been done over the last years, more than 80 % of the overall contamination by EMs at firing positions were found in the first 10 cm of soil. That represents a concern for DND since military personnel can be exposed to these compounds which eventually may be transported to the surface waters as well as groundwaters. Currently, there is no official protocol for routinely removing explosive residues from surface soils. If a procedure were implemented, the future impacts to groundwater could be reduced.

This report presents the results of trials made to find a method that allows the destruction of energetic materials by heating the soil above the decomposition temperature of energetic materials in the surface and sub-surface soil. This would be an alternative method to the prescribed burns of vegetation. The goal was to determine whether fuel combustion on the surface would be sufficient to raise temperature beyond the thermal decomposition temperature of the compounds of interest (energetic materials). Soils contaminated with explosives residues (taken from a contaminated firing point) were analyzed for their content in nitroglycerine before and after combustion of selected fuels on the soil surface.

**Results:** The results confirmed that much of the heat produced during combustion of various fuels is directed upwards and that sands acts as an isolation barrier, preventing the destruction of EMs in the deeper layers of soil. The use of a thicker layer of combustible did not increase the temperature as the unburned fuel acted as an isolating barrier. The most promising fuel was the gelled ethanol (Gelled fuel, Home Presence by Trudeau, Montreal, QC). When mixing the first cm of soil with the gel in a 1:1 v/v proportion, a temperature of > 190°C at 1 cm below the soil surface was reached.

The concentration of nitroglycerine in soil taken from the firing position of an anti-tank firing range was monitored before and after the combustion of selected fuels. Soil

samples were extracted and NG was analyzed by HPLC. The concentration of NG showed a reduction for most of the thermal treatments, but only in the surface soils (0-1 cm). Gelled ethanol offers the most interesting results, with a decrease of 76 and 53 % when placed directly over soil for two separated trials. The best performances were obtained with the same commercial gelled ethanol, but when the gel was mixed with the first layer of soil : the reduction for NG was over 90 % for the two trials.

**Significance:** The remediation of contaminated soils by energetic materials may be done using this thermal procedure involving the combustion of ethanol-based gelled fuel. When mixing the uppermost layer (0-1 cm) of soil with the gel, important reduction of NG is possible.

**Future plans:** The next step would be to use the most promising fuel, i.e. the gelled ethanol on a range in real conditions, such as soil humidity, heterogeneous soil, winds, etc. to determine if the controlled burning of a gelled fuel is an alternative for soil decontamination that may be used on a large scale. This work has been carried out in Autumn 2009 on a Canadian Forces Base (Gagetown) and will be the subject of a future report.



## Sommaire

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### **Development of a remediation strategy for surface soils contaminated with energetic materials by thermal processes: Phases 1, 2 and 3**

**Isabelle Poulin; Gaston Nadeau, Annie Gagnon; DRDC Valcartier TR 2009-150; R & D pour la défense Canada – Valcartier; Novembre 2009.**

**Introduction ou contexte:** Afin d'assurer un haut degré de préparation des troupes militaires pour toute mission, une partie importante de l'entraînement est constituée d'exercices de tir à feu réel. Une conséquence de cet entraînement est la contamination de plusieurs sites par des matériaux énergétiques (ME). Des résidus de poudre propulsive s'accumulent aux positions de tir et le matériel de remplissage des obus et projectiles peut être répandu autour des cibles, par exemple lorsqu'une munition non explosée est fracturée après avoir été frappée par des éclats et fragments d'obus.

Pour la plupart des champs de tir canadiens où la caractérisation environnementale a été effectuée au cours des dernières années, plus de 80 % de la contamination des positions de tir par les explosifs se retrouve dans les premiers 10 cm de sol. Cela est inquiétant pour le ministère de la Défense nationale puisque le personnel militaire peut être exposé à ces composés qui peuvent être transportés dans les eaux de surface et souterraines. Présentement, il n'existe pas de protocole officiel utilisé de façon régulière pour enlever les résidus d'explosifs des sols de surface. Si une procédure était mise en oeuvre, les impacts futurs sur l'eau souterraine pourraient être diminués.

Ce rapport présente les résultats de tests effectués pour trouver une méthode qui permettrait de détruire les matériaux énergétiques en augmentant la température du sol au-dessus de leur température de décomposition à la surface et dans la sous-surface du sol. Cette méthode serait une solution de rechange aux brûlages contrôlés de végétation. Le but était de déterminer si une combustion de divers carburants sur la surface est suffisante pour provoquer une hausse de température au-delà de la température de décomposition des composés d'intérêt (matériaux énergétiques). Des sols contaminés par des résidus d'explosifs pris à un pas de tir contaminé ont été analysés pour leur contenu en nitroglycérine (NG) avant et après la combustion de certains carburants sélectionnés sur la surface du sol.

**Résultats:** Les résultats confirment que la plus grande partie de la chaleur produite durant la combustion des divers carburants est dirigée vers le haut et que le sable agit comme barrière isolante, prévenant la destruction des MEs dans les couches plus profondes du sol. L'utilisation d'une couche plus épaisse de carburant n'augmente pas la température, puisque la partie intacte agit comme isolant. Le carburant le plus prometteur est un gel à base d'éthanol (Gelled fuel, Home Presence by Trudeau, Montreal, QC). Lorsque

mélangé avec le premier cm de sol dans une proportion 1 :1, la température atteinte est > 190°C à 1 cm sous la surface.

La concentration de nitroglycérine dans le sol provenant d'un pas de tir d'un site anti-char a été mesurée avant et après la combustion des carburants sélectionnés. Les échantillons de sol étaient extraits et la NG a été analysée par HPLC. La concentration en NG montre une réduction pour la plupart des traitements, mais seulement en surface (0-1 cm). Le gel à base d'éthanol offre les résultats les plus intéressants, avec une baisse de 76 % et 53 % lorsque le gel est placé directement sur le sol (deux essais distincts). Les meilleures performances ont été obtenues avec le même gel commercial, mais en mélangeant le gel avec la première couche de sol. La réduction en NG est supérieure à 90 % pour tous les essais.

**Importance:** La restauration de sols contaminés par les matériaux énergétiques pourrait être faite en utilisant un procédé thermique qui implique la combustion d'un gel à base d'éthanol. Lorsque mélangé avec la couche superficielle du sol (0-1 cm), une importante diminution de la quantité de NG est possible.

**Perspectives:** La prochaine étape serait d'utiliser le carburant le plus prometteur, c'est-à-dire le gel à base d'éthanol, sur un site d'entraînement et dans des conditions variables, telles que l'humidité, l'hétérogénéité du sol, des vents, etc. et de déterminer si la combustion contrôlée du gel est une solution de rechange pour la décontamination des sols qui pourrait être utilisée à grande échelle. Ces tests ont été réalisés à l'automne 2009 sur une base des Forces canadiennes (Gagetown) et feront l'objet d'un autre rapport.

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# 1 Introduction

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To ensure a high degree of preparedness of military troops for any potential mission, training with live weapons is an important part of the military activities. As a result of this training, many ranges and training areas are contaminated with energetic materials (EM). Propellant residues accumulate at firing positions and projectiles filling may be spread near the targets, for example when an unexploded ordnance (UXO) is fractured after being hit by shrapnel or other fragments.

Environmental characterization at Canadian Forces Base/Air Support Unit (CFB/ASU) Wainwright demonstrated that soil samples from the firing positions of small arms and anti-tank ranges were contaminated with high levels of nitroglycerine (NG) [1] (for example at Range 13 - Hand Held Anti-Tank Stationary Target, the first 2.5 cm of soil of the firing position were found to be contaminated with 4500 mg/kg of NG). For many ranges studied, the contamination by EMs was not only present on the top surface, but was also in deeper layers. On some Canadian bases, the contamination was found up to 60 cm deep, but it has to be noted that, for all the sites studied, more than 70 % of the overall contamination was found in the first 20 cm of soil [2]. That represents a concern for DND since military personnel can be exposed to these compounds which eventually may be transported to surface and groundwaters. Migration of EM to waters is not only a hypothetical risk : in 1997, the U.S. Environmental Protection Agency (USEPA) issued Administrative Order No. 2 to the National Guard Bureau and the Massachusetts National Guard requiring that certain training activities (artillery and mortar firing) cease, pending the completion of environmental investigations at the training ranges and impact area. In January 2000, the USEPA, Region I, issued Administrative Order 3, which, in brief, required the suspension of military training because of environmental contamination of soils and groundwater at Massachusetts Military Reservation (MMR) Training Range and Impact Area. Among the contaminants, lead, explosives, explosives-related compounds, pesticides and other organic contaminants were detected in soils, and cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), trinitrotoluene (TNT), cyclotetrametylenetetranitramine (HMX) and some organics were found in groundwater [3].

Currently, there is no official protocol for routinely removing explosive residues from surface soils in ranges and training areas. If a procedure were to be implemented, the future impacts to groundwater could be reduced. Different remediation strategies are currently studied in order to address the problem of surface soils contamination by energetic materials.

## 1.1 Objective of the work

This report will present the results of trials made to find an alternative method to the prescribed burnings of vegetation by heating the soil enough to decompose the energetic materials in the surface and sub-surface soil. The goal was to determine whether fuel combustion on the surface would be sufficient to raise temperature beyond the thermal decomposition temperature of the compounds of interest (energetic materials). This work was separated into three phases. During

Phase 1, preliminary tests were carried out : a small quantity of contaminated soils were heated when ethanol or propane were ignited. During Phase 2, various combustible materials were tested to determine the heat propagation in sand. During Phase 3, the most promising combustibles were ignited on a medium amount of contaminated soil and the efficiency for decreasing the concentration of NG was determined.

## 2 Contextual informations

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### 2.1 Remediation strategies for explosives-contaminated soils

This section will present some techniques that can be used to reduce the concentration of explosives in soils. Some techniques are still at the development level. In Canada, neither of these activities are used on a regular basis for soil remediation. This non-exhaustive list of biological treatment technologies is taken from the US Federal Remediation Technologies Roundtable, which published in 2008 the Remediation Technologies Screening Matrix and Reference Guide, that can be found in Reference [4].

Biological treatment, or bioremediation, is a developing technology that uses microorganisms to degrade organic contaminants into less hazardous compounds. Bioremediation is most effective for dilute solutions of explosives and propellants. TNT in the crystalline form is difficult to treat biologically.

Trinitrotoluene degrades under aerobic conditions into monoamine-, diamino-, hydroxylamine-DNT, and tetranitro-azoxynitrotoluenes. RDX and HMX degrade into carbon dioxide and water under anaerobic conditions. Researchers have not identified any specific organisms that are particularly effective for degrading explosives waste; an indigenous consortium of organisms usually affects the degradation.

The US Department of Defense (DOD) is currently developing or implementing six biological treatments for explosives-contaminated soils: aqueous-phase bioreactor treatment, composting, land farming, phytoremediation, white rot fungus treatment, which are solid-phase treatments, and in situ biological treatment.

- Aqueous Phase Bioreactor Treatment: DOD is considering two types of aqueous-phase bioreactors for the treatment of explosive contaminants. The first is the lagoon slurry reactor, which allows contaminants to remain in a lagoon, be mixed with nutrients and water, and degrade under anaerobic conditions. The lagoon slurry reactor is still at the development stage. The second is the aboveground slurry reactor, which is either constructed on-site or purchased as a package plant.

Aqueous-phase bioreactors provide good process control, can be configured in several treatment trains to take care for a variety of wastes, and potentially can achieve very low contaminant concentrations. A drawback of bioreactor treatment is that, unlike composting systems which bind contaminants to humic material, bioreactors accumulate the products of biotransformation. In addition, bioreactors have been shown to remediate explosives only at laboratory scale, so the cost of

full-scale bioreactors will have to incorporate a variety of safety features that will add to their total cost.

- Composting: DOD has been evaluating composting systems to treat explosives waste since 1982. To date, composting has been shown to degrade TNT, RDX, HMX, DNT, tetryl, and nitrocellulose in soils and sludges. The main advantage of this technology is that, unlike incineration, composting generates an enriched product that can sustain vegetation. After cleanup levels are achieved, the compost material can be returned to the site. Another advantage is that composting is effective for a range of wastes. The cost of composting can be limited, however, by the level of indigenous organisms in contaminated soil and the local availability of amendment mixtures. In addition, composting requires long treatment periods for some waste streams, and composting of unfamiliar contaminants potentially can generate toxic byproducts.

Composting methods fall into three categories: static-pile composting; mechanically agitated in-vessel composting and windrow composting. In static-pile composting, contaminated material is excavated, placed in a pile under protective shelter, and mixed with readily degradable carbon sources. The pile undergoes forced aeration to maintain aerobic and thermophilic (55 to 60°C) conditions, which foster the growth of microorganisms. Bulking agents, such as cow manure and vegetable waste and/or wood chips, can be added to enhance biodegradation. In mechanically agitated in-vessel composting, contaminated material is aerated and blended with carbon-source materials in a mechanical composter. These devices have been used at municipal sewage treatment facilities and applied to explosives waste. Windrow composting is similar to static-pile composting, except that compost is aerated by a mechanical mixing vehicle, rather than a forced air system.

- Landfarming: Landfarming has been used extensively to treat soils contaminated with petroleum hydrocarbons, pentachlorophenol (PCP) and polycyclic aromatic hydrocarbons (PAHs) and potentially could be used to treat low to medium concentrations of explosives as well. In land farming, soils are excavated to treatment plots and periodically tilled to mix in nutrients, moisture and bacteria. In one pilot study at an explosives waste site in Hercules, California, land farming failed to achieve the target cleanup levels of 30-ppm TNT, 5-ppm DNT and 5-ppm DNB. However, the study achieved a 30 to 40 % contaminant degradation.
- Phytoremediation: The U.S. Army Environmental Center (USAEC) is developing technologies to effectively clean up contaminated soil with residues of explosives such as TNT, RDX, HMX and DNT. One potential treatment alternative is phytoremediation using constructed wetlands. Phytoremediation is a process which uses plants to degrade, not uptake, explosives. Once this process is proven in constructed wetlands, it could be applied in natural wetlands to remediate explosives-contaminated groundwater. Constructed wetlands have already proven to

be effective for treating acid mine drainage and municipal waste waters. Wetlands phytoremediation is a technology that is relatively self-sustaining and cost-effective to maintain. In addition, this technology does not produce secondary waste streams.

In bench-scale testing, the EPA National Exposure Research Laboratory in Athens, GA, has identified a plant nitroreductase enzyme shown to degrade TNT, RDX and HMX in concert with other plant enzymes. An immunoassay test has been developed that identifies nitroreductase activity in a wide variety of aquatic and terrestrial plants. This opens a door to a variety of potential applications for cleanup using plants in wetlands.

- White Rot Fungus Treatment: White rot fungus, *Phanerochaete chrysosporium*, has been evaluated more extensively than any other fungal species for remediating explosives-contaminated soil. Although white rot has been reported in laboratory-scale settings using pure cultures, a number of factors increase the difficulty of using this technology for full-scale remediation. These factors include competition from native bacterial populations, toxicity inhibition, chemical sorption and the inability to meet risk-based cleanup levels.

In bench-scale studies of mixed fungal and bacterial systems, most of the reported degradation of TNT is attributable to native bacterial populations. High TNT concentrations in soil also can inhibit the growth of white rot fungus. One study suggested that *Phanerochaete chrysosporium* was incapable of growing in soils contaminated with 20 ppm or more of TNT. In addition, some reports indicate that TNT losses in white rot fungus studies can be attributed to adsorption of TNT onto the fungus and soil amendments, such as corn cobs and straw.

- In Situ Biological Treatment: In situ treatments can be less expensive than other technologies and produce low contaminant concentrations. The available data suggest, however, that in situ treatment of explosives might create more mobile intermediates during biodegradation. In addition, biodegradation of explosive contaminants typically involves metabolism with an added nutrient source, which is difficult to deliver in an in situ environment. Mixing often affects the rate and performance of explosives degradation. Finally, effectiveness of in situ treatment is difficult to verify both during and after treatment.

Other examples of bioremediation can be found in Reference [5], where Daramend®, a proprietary organic bioremediation product, was applied ex situ on soil contaminated with nitroaromatic explosive compounds. The soil was mixed, aerated and homogenized with the product. Water was applied to increase the soil moisture. The treatment was repeated six times, every 7 to 10 days and the mean RDX concentration was reduced by almost 99 %, while the mean concentration of HMX was reduced by 92.4 %.

Thermal treatment technologies for explosives also exists [4], such as hot gas decontamination and incineration (by rotary kiln incinerator, deactivation furnace, and contaminated waste processor). Other techniques, such as soil washing, are being developed, but they produce secondary wastes. The use of lime to induce alkaline hydrolysis of explosives in soils is also being studied as a remediation strategy [6].

The use of fire ecology—the science of using fire to manage vegetation and ecosystems—has also been investigated as an innovative approach to destroy explosives residues in surface soils [7]. For target areas, where vegetation is present, controlled or prescribed burning as a management technique can be used for a variety of purposes: safety clearance prior to detection and destruction of UXO, wildfire avoidance, and plant and wildlife management. These fires have the potential to destroy energetic compounds - which are either associated with the vegetation that is burned or are in or on the surface soils which are heated by the fire – if they are exposed to temperatures above the thermal decomposition temperature as the flames propagate. Still, more information is needed to evaluate the destruction of explosives residues by fire and a better understanding of the underlying processes of sublimation, and melting/migration of the explosives residuals is needed. Since many of the contaminated firing positions are not covered with vegetation, alternative burning procedures to the ignition of dry grass or other vegetation should be considered.

## **2.2 Decomposition of energetic materials**

Explosives undergo thermal decomposition at temperatures far below those at which spontaneous explosion may occur. A considerable amount of energy in the form of heat is liberated in the decomposition process. This highly exothermic reaction accelerates to a high velocity culminating in deflagration or detonation when the rate of heat production is greater than the rate of heat loss to the surroundings by conduction and convection. Explosives in their normal state are metastable, the free energy of the explosive being considerably higher than its decomposition products. For an explosive to remain stable at ordinary temperatures, its decomposition reaction must depend on relatively high activation energies [8].

## 2.3 Controlled burnings

A team of US scientists has carried out work on controlled burnings, both in the laboratory and on military training ranges [9]. From laboratory testing, the following conclusions were drawn : i) the thermal decomposition of TNT and RDX is a function of temperature, concentration, soil moisture, soil chemistry and other physical properties; overall, temperatures near 250°C resulted in rapid decomposition of both TNT and RDX; ii) generally, higher temperatures and lower soil concentrations result in more rapid decomposition of TNT and RDX; iii) oxygen is required to support thermal decomposition; and iv) soil-associated TNT and RDX decompose at temperatures consistent with those observed in the field (175°C-RDX and 250°C-TNT). The field demonstration used a bed of pine needles as a combustible material to sustain the fire for the prescribed burn over a large area. From the field work, the group drew many conclusions. Among them : during controlled burning, temperatures at ground surface and above can reach levels that support rapid thermal decomposition, but heat generated during the controlled burn did not penetrate into the ground for more than a few centimetres. For example, at two different test areas, temperatures at ground surface reached near 600°C while the maximum temperatures achieved at 2.5 cm below grade were 96°C and 52.5°C. They also observed that there was no temperature effect at 8.5 cm below ground surface at any of the test area locations. They demonstrated that pine straw burns hot, is effective at carrying a burn, but is not effective at heating the subsurface soil. Previous research has shown that heat penetration into soil is a function of both the intensity and duration of the fire. The pine straw burned too rapidly heating the ground surface for less than 10 minutes in most cases, which was not of sufficient duration to heat the soil. Temperature data suggested that thicker beds of needles acted as an insulator as the flames propagate. The increased fuel loading appeared to lower the temperature of the burn on the underside of the needle bed.

The work of Hubbard et al. [10] on prescribed burnings in a oak-pine forest also demonstrated that the heat penetration in soil was low: during a burning of maximum flame temperature of 344°C, the temperature at 2.0 and 1.0 cm was 45 and 59°C, respectively. Some authors [11] inferred the temperature beneath the surface during burnings using the temperature histories reported by Frandsen and Ryan [12], which show a decrease in peak temperature of about 200°C between thermocouples positioned at the dry mineral soil surface and those positioned 2 cm below the mineral soil surface.

Also, Hubbard et al. [10] demonstrated that neat TNT can migrate downward into the soil profile if temperatures are not sufficiently high to rapidly decompose TNT: melting occurs. Neat RDX does not have the same propensity as TNT to melt and migrate into the soil. The melting point temperature for RDX is closer to its decomposition point, 204°C versus 260°C, respectively [13]. The overall conclusion from the investigation was that using prescribed burning on ranges has potential for destroying a significant amount of explosives residual in surface soils and plant tissues, but additional work was needed to better understand different parameters and improve the design of the burn to increase the transfer of heat to the soil profile.

### **3 Phase 1 : Preliminary tests**

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In Phase 1, small-scale laboratory experiments involving contaminated soils were conducted. Two common fuels, ethanol and propane, were tested as combustible agents and the concentration of NG was measured in a soil sample before and after burning. This phase was carried out in March 2008.

Soils samples collected in 2005 at CFB/ASU Wainwright were used. A high number of these soils samples were analyzed in 2005 and this information guided us in the choice of specific samples for this study. The chosen soils all exhibited a concentration of NG over 15 mg/kg (dry soil) and were taken from firing points (Ranges 5 and 20, see [1] for details on the ranges and sampling procedure).

#### **3.1 Experimental method**

This section will present the experimental work carried out to determine the efficiency of destruction of NG when two different fuels, propane and ethanol, are burned over contaminated soil. Soil preparation, burning procedure and sample analysis will be presented in this section.

##### **3.1.1 Soil preparation**

In 2005, after their collection, the soil samples were air-dried in the dark, and homogenized by adding acetone to form a slurry, which was then evaporated. Homogenized soils were sieved through 25-mesh sieves. They were then kept in plastic bags in the dark at room temperature. Once dried, the samples are stable. They were used without other preparation.

For these experiments, the use of a sieved soil prevented the presence of large chunks of energetics, and eliminated the risk of explosion as the critical diameter was not reached for any of the particles.

For each process studied, combustion of propane and ethanol, two blanks (uncontaminated Ottawa sand, named B1 to B4) were used, plus three soils samples (named with numbers from 1 to 6). The burnings were carried out at a small-scale level. The preparation of the sample and the burning were performed in separate laboratories. A mass of 100 g of each soil was placed in a plastic bag and identified. These samples were then brought to the test site.

For both series of tests, the content of each plastic bag was poured into its identified pyrex vessel (21 x 21 x 5 cm) and spread uniformly. A mass of 10 g was removed by taking 20-increment sub-



samples. This material was extracted and analyzed for NG by High Performance Liquid Chromatography (HPLC). One clean pyrex vessel was used for each soil sample to minimize the risks of cross-contamination.

### **3.1.2 Burnings**

The two burning procedures tested are presented in the following paragraphs.

#### **3.1.2.1 Propane burnings**

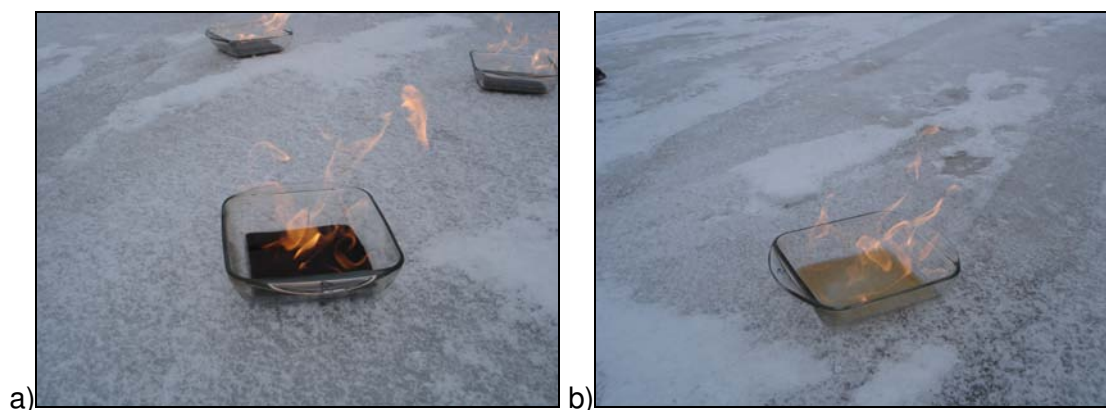
The pyrex vessel was placed in a fume hood and the flame of a lighted propane torch (as used for small-scale welding) was moved on the soil for 5 min, as shown in Figure 1. The sand was gently moved in the pyrex to optimize flame contact. After 5 min, the pyrex was covered with an aluminium foil and let to cool down. The soil was transferred to a clean plastic bag and brought back to the laboratory for analysis.



*Figure 1: Burning of a soil sample with a propane torch*

### 3.1.2.2 Ethanol burnings

These tests, since they involve a naked flame, were done outdoors. A volume of 100 mL of ethanol was poured over the soil in the pyrex vessel. This volume was chosen because it was enough to cover the surface of the container. Ethanol was ignited using a long BBQ lighter. The setup is shown in Figure 2. It took about 3 minutes to burn the ethanol completely. Once cooled, the soil was transferred to a clean plastic bag and brought back to the laboratory for analysis.



*Figure 2: Burning with ethanol; a) contaminated soil, b) Ottawa sand*

### 3.1.3 Sample analysis

A 10-g aliquot of soil, composed of 20-increment sub-samples, was taken out of the plastic bag and put into a 30-mL amber vial and mixed with 20 mL of acetonitrile (ACN). A vortex was applied for 1 min, followed by sonication for 18 h in an ultrasonic bath in the dark. The samples were left to settle for 30 min. ACN (0.7 mL) was recovered from the vial and diluted with water (0.7 mL) containing calcium chloride (1 % w/w). The solution was filtered on a 0.45- $\mu$ m filter to get 1 mL of solution for injection on the HPLC.

Soil extracts were maintained at 4°C until analyzed by HPLC according to an in-house method derived from EPA Method 8330b [14]. All analyses were performed with an HPLC Agilent HP 1100 equipped with a degasser G1322A, a quaternary pump model G1311A, an autosampler G1313A, and an ultraviolet (UV) diode array detector model G1315A monitoring at 205, 230 et 250 nm. The injection volume was 20  $\mu$ L and the column used was a Supelcosil LC-8 column 25 cm x 3 mm x 5  $\mu$ m eluted with 15:85 isopropanol/water (v/v) at a flow rate of 0.75 mL/min. The column temperature was maintained at 25°C during the analysis. As for samples, standards and solvents were diluted 1:1, acetonitrile to water before injection.

## 3.2 Results

*Table 1 : Results for NG in soil samples for two small-scale burnings (Phase 1)*

Thermal process	Soil sample	[NG] (mg/kg) before	[NG] (mg/kg) after	Reduction (%)
Burning with propane	B1	nd	nd	--
	B2	nd	nd	--
	1	15.1	3.1	80
	2	22.4	4.0	82
	3	21.7	4.6	79
Burning with ethanol	B3	nd	nd	--
	B4	nd	nd	--
	4	15.0	3.3	78
	5	32.6	3.8	88
	6	27.4	2.4	91

nd = not detected

NG was not detected before or after the burnings in blanks. Cross contamination is therefore not considered to be possible (or too low to be detected).

This small-scale study has shown promising results for remediation of surface soils in ranges contaminated by nitroglycerine that exhibit no vegetation cover. The increase in soil temperature by using a propane torch or by lighting ethanol seems to be very efficient in decreasing the concentration of NG in soils. The average reduction of NG when burning with a propane torch is  $80 \% \pm 2$  where the burning with ethanol is  $86 \% \pm 7$ . Even though propane gives promising results, this mean of heating the soil will probably be too difficult to implement on a real site where UXO may be found and where the burning will be carried out without any personnel nearby.

Future work will try to answer these two questions :

1) If the solvent is not confined in a shallow vessel, will it drain through the soil and be impossible to ignite ?

In order to answer this question, deeper vessels (20 cm) will be filled with sand (commonly present on the ranges) and a small quantity of combustible material will be used. Different combustible materials, with various viscosities will be studied.

2) If the contamination is not confined to the first cm of soil, will the heat go deep enough to decompose the energetic residues ?

To answer this question, thermocouples will be placed at different depths and temperature will be measured during the combustion of the various materials.

## **4 Phase 2 : Determination of the heat propagation in sand during the burning of various fuels**

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The aim of this part of the work was to determine the efficiency of penetration of heat in soil during controlled burns. Various fuels were poured or spread on the soil and ignited. Thermocouples were used to record the temperature at different depths: 1, 2, 5 and 8 cm below the surface. These tests were carried in September 2008.

### **4.1 Experimental method**

#### **4.1.1 Material for temperature measurements**

In this study, uncontaminated sand (Silica sand, Temiska Inc.) was used as a substrate. Sand is often found in Canadian training ranges. Aluminium containers (20 x 20 x 20 cm) were used to hold the sand. The use of a deep container, as compared with a pyrex plate in Phase 1, allowed us to use a larger quantity of sand.

On the container, a line was drawn at about 14 cm (from the bottom of the container), to indicate the level up to which the container will be filled with sand. Marks were indicated at 1, 2, 5 and 8 cm below the top sand level. Holes were drilled to insert thermocouples in the container. The thermocouples (type J, see Figure 3) were placed in the container with the sensing end placed in the center of the box (Figure 4). The thermocouples were kept parallel to the bottom of the container with an improvised stand, as seen in Figure 5.



*Figure 3: Aluminium containers for the burnings and thermocouples*



*Figure 4 : Thermocouples inserted in the container, the arrow indicates the sensing end in the middle of the container*



*Figure 5 : Thermocouples in the sand box. They are kept parallel to the bottom of the container with an improvised stand.*

#### **4.1.2 Fuels tested**

Various combustible materials (fuels) were tested, in order to determine 1) if it is possible to ignite the material or if it goes through the soil pores and drains to the bottom of the container, and 2) the heat propagation in the soil at various depths.

The fuel choice was dictated by many criteria : i) any unburned material should be non-toxic to the environment (wildlife and plants); ii) material should be easy to manipulate; iii) it should be possible to spread out the combustible material and ignite it after. This last criterion will become important in a real-range situation where it will be necessary for security reasons to ignite the combustible remotely. The chosen fuels are presented in Table 2.

*Table 2 : Chosen fuels for the tests (Phase 2)*

Ethanol
Methanol
Isopropanol
Wood shavings
Wood shavings soaked with ethanol
Gelled methanol (Cooking gel fuel, Magic Flame, Scientific Utility Brands International Inc. London, ON) (see Figure 6a)
Gelled ethanol (Gelled fuel, Home Presence by Trudeau, Montreal, QC) (see Figure 6b)
Home-made ethanol gel (prepared in the laboratory with calcium acetate and water)



Figure 6 : Gelled fuels: a) methanol; b) ethanol

### 4.1.3 Burnings

The sand was dried in an oven at 100°C before the experiments. Once back to room temperature, one aluminium container was filled with the sand, and the thermocouples were inserted parallel to the bottom of the container in the sand until the sensing end was in the middle of the box. The thermocouples were then connected. The combustible was spread or poured on the sand surface and the data acquisition was started. The data acquisition was controlled remotely with a Labview-based software. The user interface is shown in Figure 7. The laboratory in which the tests were carried out is usually used for trials and experiments that present a danger to the personnel security, so the laboratory and the control room are separated by a concrete wall. The burnings were observed through a video camera. A picture of the control room is presented in Figure 8. Starting from the right, the second screen is a small TV monitor to which the images taken by the video camera were sent.

Once the data acquisition was started, one member of the work team went to the laboratory and ignited the fuel using a propane torch held on a long wood stick (see Figure 9). Right after the ignition, all the personnel stayed in the control room until no flames were seen on the monitor. The data acquisition was kept on for many minutes after the end of the burning.

Four aluminium containers were used in rotation for the burnings, to ensure that the sand was cool at the beginning of the data recording.



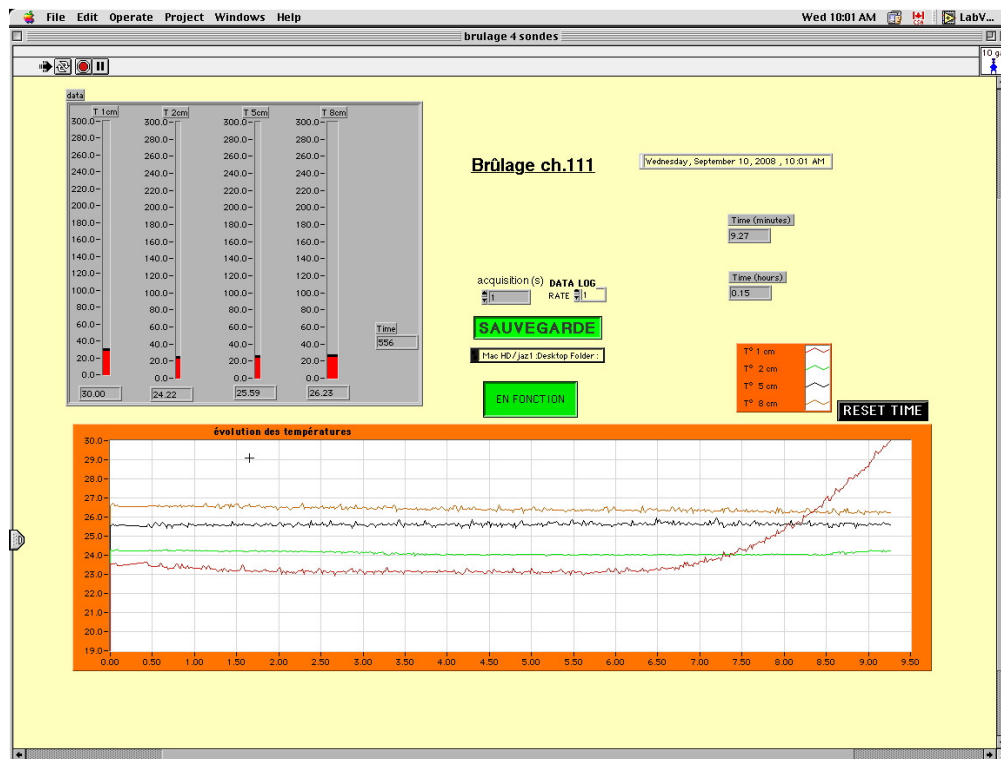


Figure 7 : User interface for the thermocouple's control panel

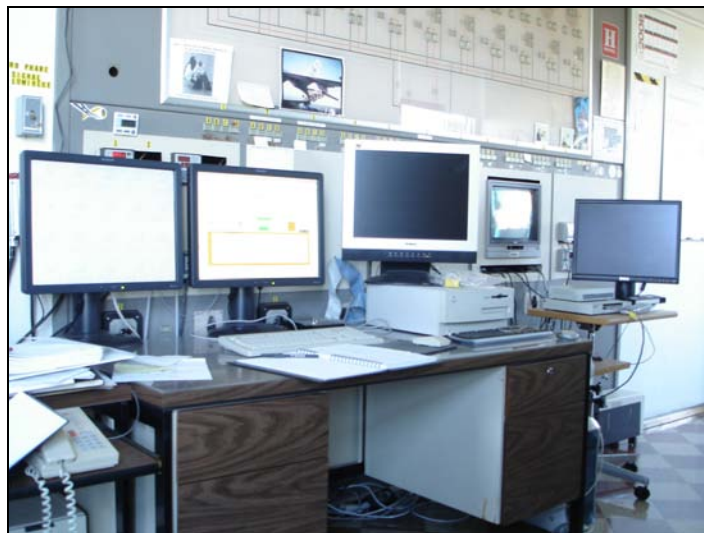


Figure 8 : Control room



*Figure 9 : Propane torch used for the ignition of the fuel*

## 4.2 Results

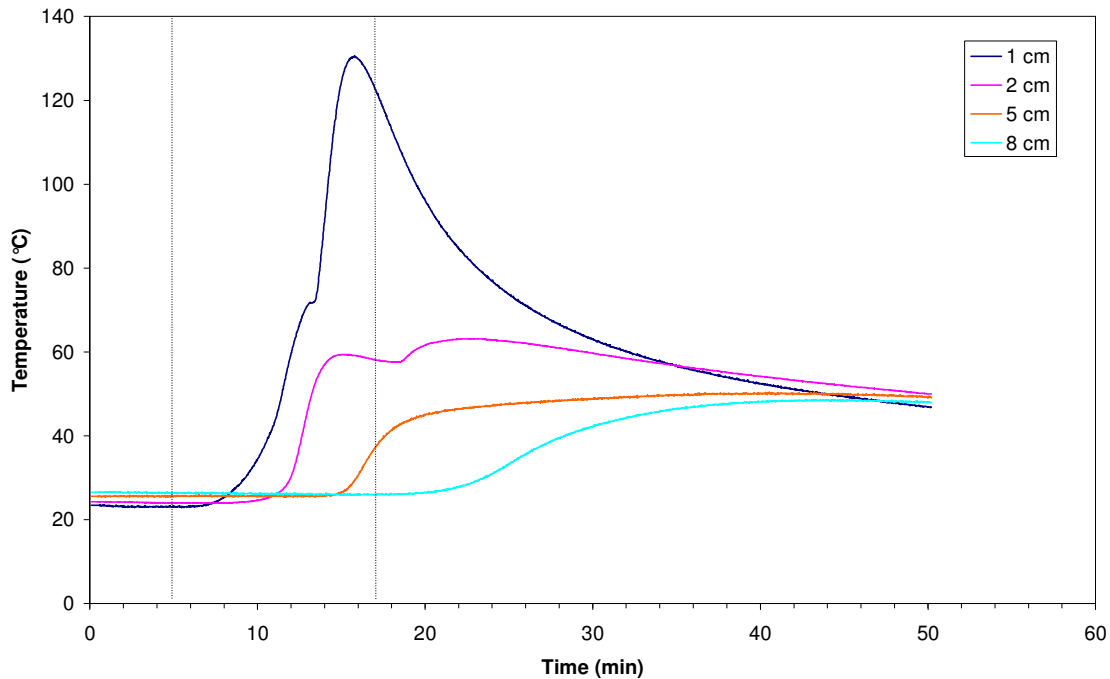
This section presents the results of the temperature measurements by the thermocouples at different depths in the sand during combustion of various fuels. The results are presented on graphs where the beginning and the end of the burning is indicated by vertical grey lines.

### 4.2.1 Gelled ethanol

The product referred as “gelled ethanol” in this report was a commercial product called “Gelled Fuel”, manufactured by the Home Presence by Trudeau Company. This product was sold to be used in fondue burners. The MSDS of this product indicated that the ingredients are ethanol (75-95 %) and methylethylketone (5 %). Water is added to complete the formulation. We are very sceptical with this information, as methylethylketone is not known to be a thickening agent. A dab of gel was left to dry and the residue was analyzed by Fourier-transformed infrared (FT-IR) spectrometry. Hydroxypropylmethyl cellulose was found to be the main component in the residue. This product probably acts as the thickening agent. The spectra of both the residue and pure hydroxypropylmethyl cellulose can be found in Annex A.

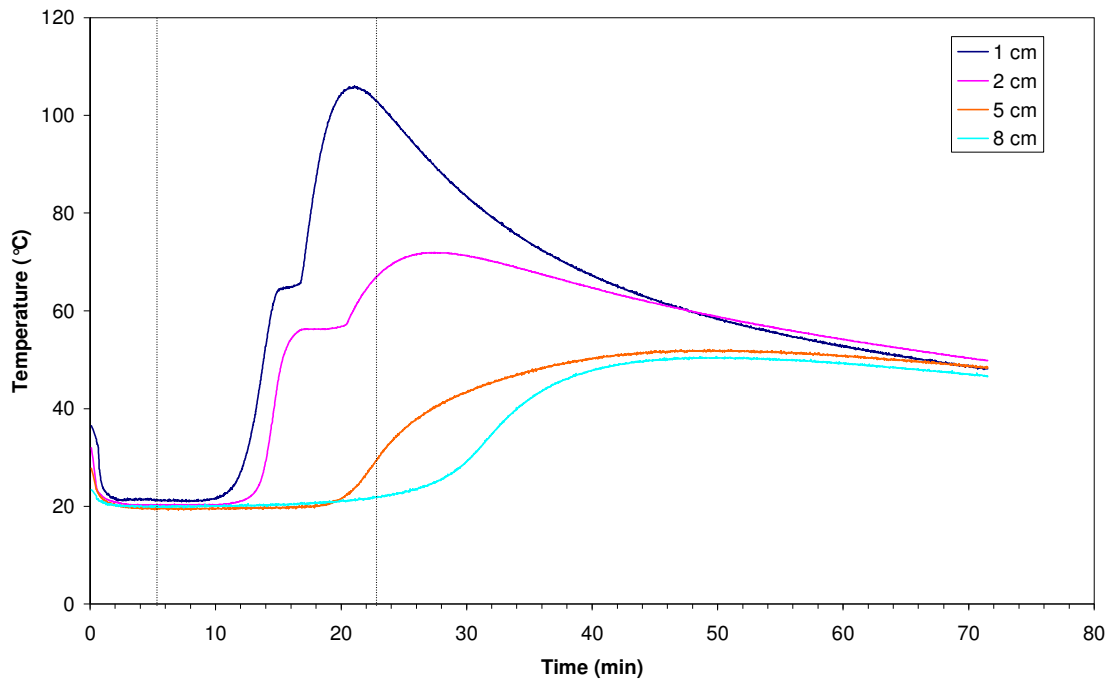
For the first test, 500 mL of gelled ethanol was spread on the sand. It gave approximately 1.25 cm thick of gel on the sand. The burning began 5 minutes after the beginning of the data acquisition and lasted for approximately 12 minutes. The recorded temperatures are presented in Figure 10. The first dashed line indicated the ignition of the gel, the second dashed line indicated when the fire went off. The maximum temperature measured at 1 cm below the surface was around 130°C. This temperature was obtained just before the fire went off. The temperatures recorded deeper in

the sand were much lower than at 1 cm: 63, 50, 49°C at 2, 5 and 8 cm, respectively. This indicated clearly that most of the heat is directed upwards and that sand acts as an insulation barrier. The thicker this barrier, the lower and slower the heat penetration, as it can be observed by the slight temperature increase for deeper thermocouples. The steps observed before the maximum temperature is reached is still not explained at this moment. It was seen for many fuels tested.



*Figure 10 : Temperatures at different depths during the combustion of 1.25 cm thick of gelled ethanol*

A second test was made as a duplicate for this experiment, and the results are presented in Figure 11. The fire lasted for a longer time, and the maximum temperature at 1 cm below the sand surface was around 106°C. It is not clear at this point what happened to cause this important difference in temperature.



*Figure 11 : Temperatures at different depths during the combustion of 1.25 cm thick of gelled ethanol (duplicate)*

A third test was carried out with the gelled ethanol, but this time with twice the amount of gel (1 L vs 500 mL), giving a thickness of 2.5 cm. The burning lasted for approximately 27 minutes. The maximum temperature obtained at 1 cm below the surface was around 80°C, while temperatures of 68, 61 and 57°C were obtained at 2, 5 and 8 cm. As compared with the first experiment with only 1.25 cm thick of gel, the increase in temperature was lower because the thicker layer of gel acted as an insulating barrier. There is thus no gain in using a higher load of gel.

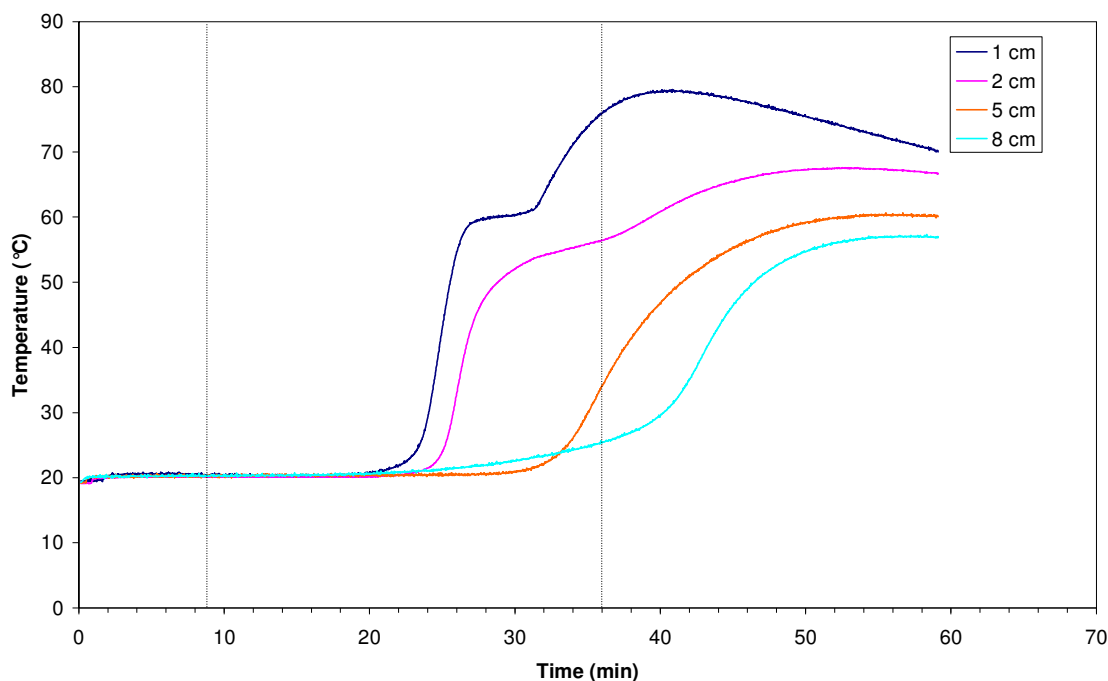


Figure 12 : Temperatures at different depths during the combustion of 2.5 cm thick of gelled ethanol

#### 4.2.2 Gelled methanol

The product referred as “gelled methanol” in this report was a commercial product called “Magic Flame”, manufactured by Scientific Utility Brands International Inc. It was sold to be used for cooking and/or heating, for example in recreational activities such as camping. The MSDS of this product indicated that the product was composed of 71 % methanol. The company told us that the other compounds are water, triethylamine and coagulum [15]. It was not possible to have more information from the vendors.

For the test, 400 g of gel (two containers) were poured on the sand. This gave around 1 cm thick of gel on the sand. The burning began 15 minutes after the beginning of the data acquisition and lasted for approximately 15 minutes. The recorded temperatures are presented in Figure 13. The first dashed line indicates the ignition of the gel, the second dashed line indicates when the fire went off. The maximum temperature measured at 1 cm below the surface was around 90°C. This temperature was obtained just before the fire went off. The temperatures recorded deeper in the sand were much lower than at 1 cm : 57, 53 and 53°C at 2, 5 and 8 cm, respectively. As for the gelled ethanol, this indicated clearly that much of the heat was directed upwards and that sand

acts as an insulation barrier. The highest temperature recorded at 1 cm below the surface (90°C) was lower than the one recorded for the gelled ethanol (130°C). This could be explained with the fact that methanol produces less energy during combustion as compared to ethanol : 17.9 vs 23.5 MJ/L [16].

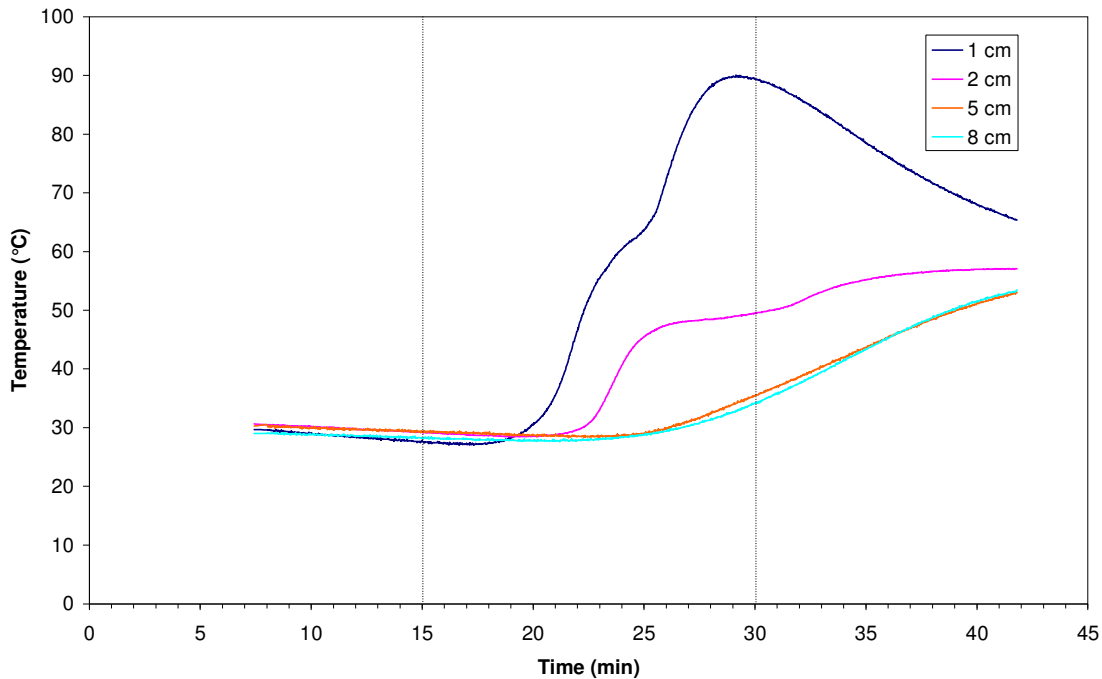
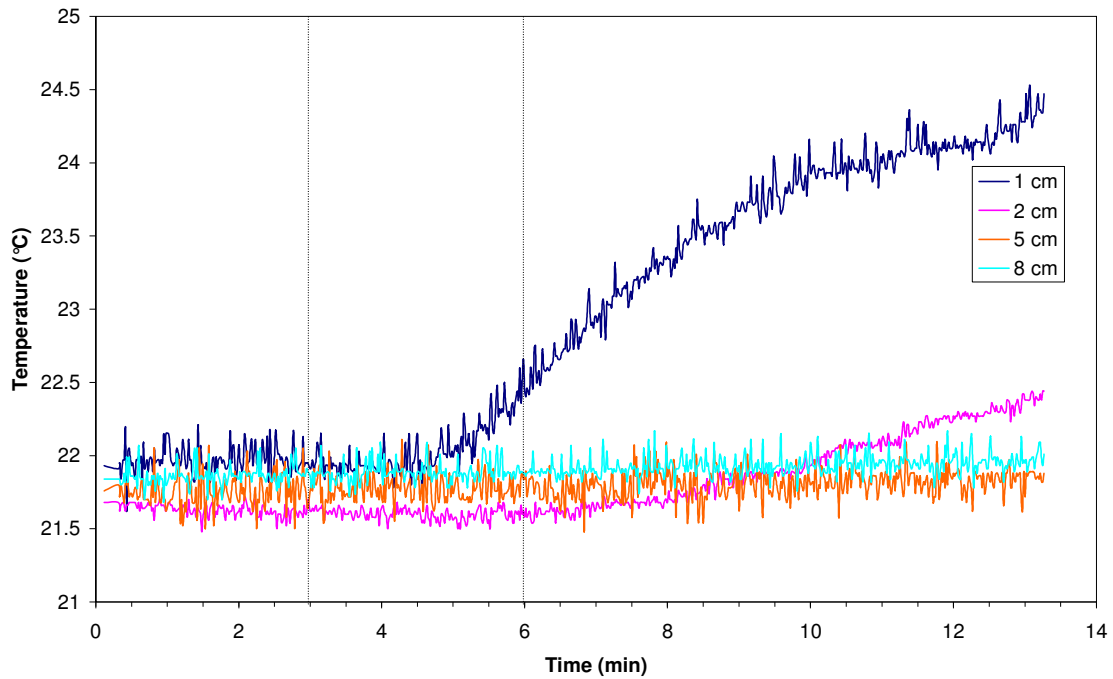


Figure 13 : Temperatures at different depths during the combustion of 1 cm thick of gelled methanol

#### 4.2.3 Wood shavings

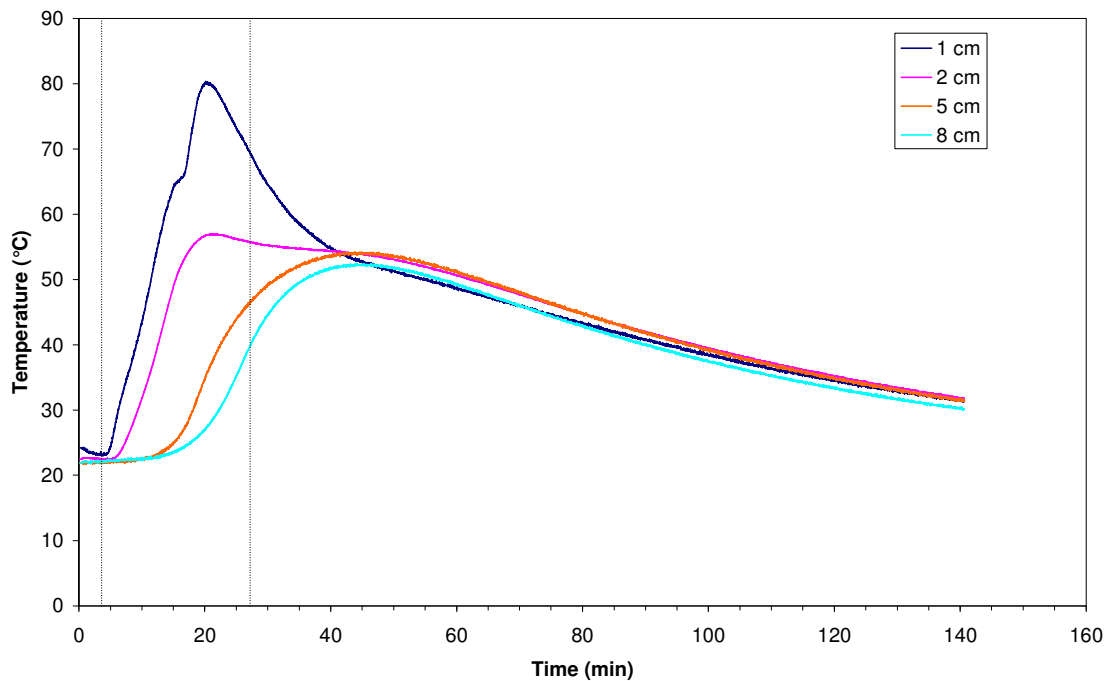
For this test, a 1L beaker was filled with pine wood shavings and then poured over the sand. The shavings were slightly packed in the beaker. Once on the sand, the final height of wood was 3.8 cm. As for the other trials, the fuel was ignited with the propane torch, but in this case, many spots were ignited. Even with this procedure, the fire lasted for less than 5 minutes, and could not burn all the wood: more than 2 cm of wood was still intact under the soot layer. The increase in temperature at 1 cm below the sand surface was negligible (see Figure 14).



*Figure 14 : Temperatures at different depths during the combustion of 3.8 cm thick of wood shavings*

#### 4.2.4 Ethanol soaked wood shavings

In order to increase the ease with which wood shavings burn, they were soaked with ethanol (500 mL of ethanol for 1 L of wood shavings, approximately 3.8 cm thick of shavings). Ignition with propane torch was made at only one position, and the fire lasted for about 20 minutes. At the end, there was still a small quantity of unburned wood under the soot layer. When the fire ended, there was about 0.5 cm of unburned wood below the soot in the middle of the container, and even more (between 1 and 2 cm) closer to the edges. The temperatures measured in the sand are shown in Figure 15. The highest temperature recorded was 80°C, at 1 cm below the surface.

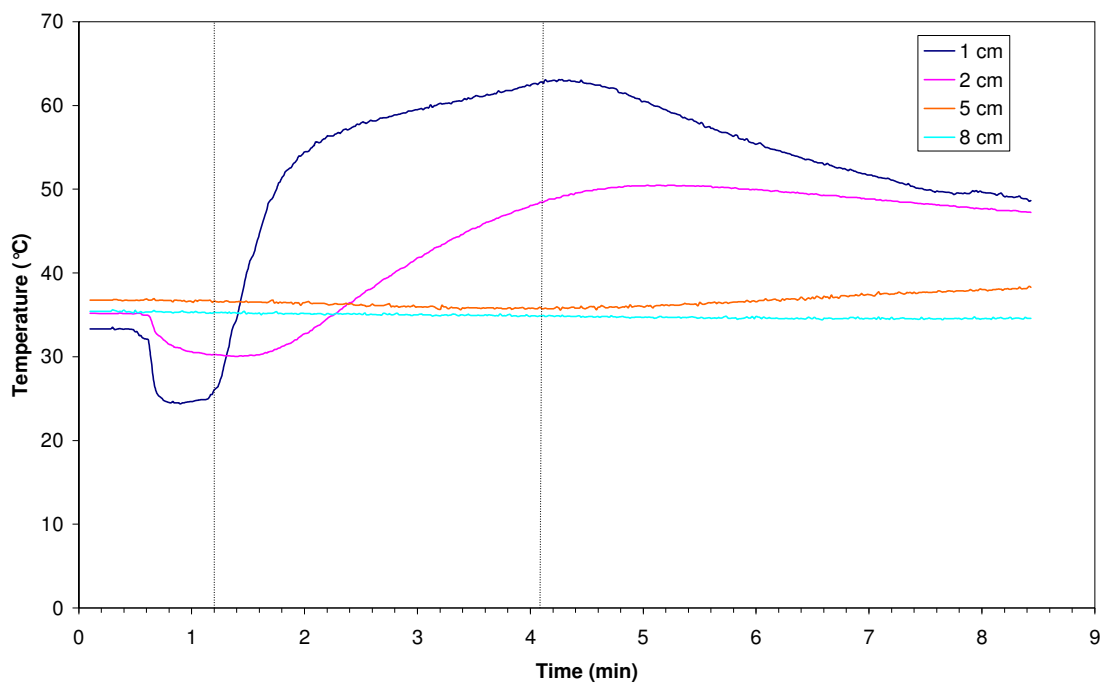


*Figure 15 : Temperatures at different depths during the combustion of 3.8 cm thick of wood shavings soaked with ethanol*

#### 4.2.5 Ethanol, isopropanol, methanol

Liquid solvents, namely ethanol, isopropanol and methanol were tested. For each test, 1L of solvent was used. In the case of ethanol, the fire lasted for 3 minutes, and the maximum temperature measured at 1 cm below the surface was 63°C. The temperature measurements are presented in Figure 16. As it was expected, most of the solvent went right into the sand and soaked it. The sand was all wet at the end of the fire.





*Figure 16 : Temperatures at different depths during the combustion of 1L of ethanol*

The other solvents tested, isopropanol and methanol, behave in the same way as ethanol: the fire did not last for a long time (3 min for isopropanol, and about 2 min for methanol) and the increase in temperature was low in the sand (see Figures 17 and 18).

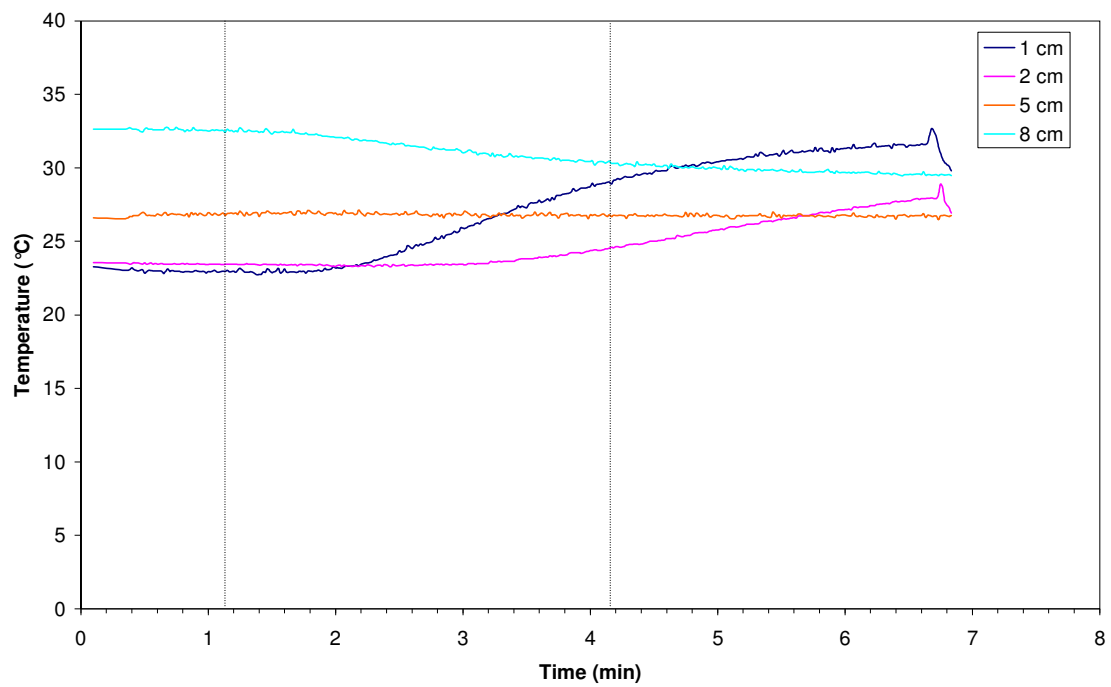


Figure 17 : Temperatures at different depths during the combustion of 1L of isopropanol

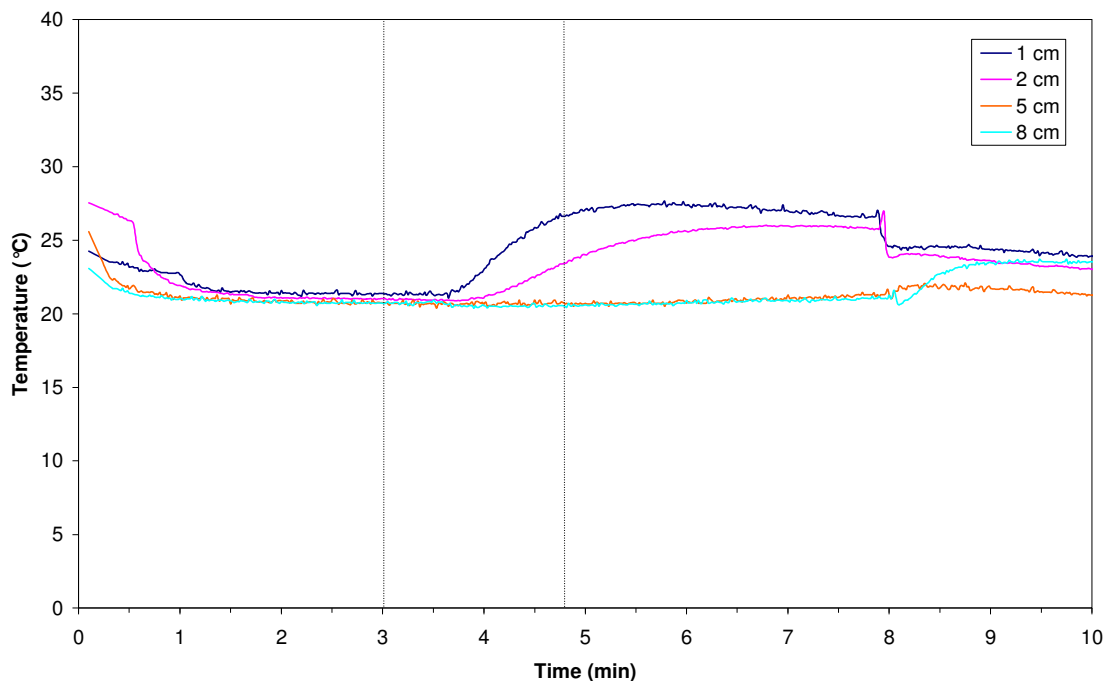


Figure 18 : Temperatures at different depths during the combustion of 1L of methanol

#### 4.2.6 Sand/gelled ethanol mix

The first results seemed to indicate that the ethanol-water gel was quite promising: the temperature at 1 cm below the surface was higher than 100°C. A test was carried out to determine if the temperature in the soil would be higher if the combustible was mixed with the first layer of sand. The first cm of sand (300 mL approximately) was removed from the aluminium container and mixed in a separate vessel with 500 mL of gelled ethanol. This mixture was then returned into the container, so that the thermocouple at 1 cm below the surface was in contact with sand (below) and sand-gel mixture (above). The fire burned for about 20 minutes and almost no residue was observed. The temperature at various depths is presented in Figure 19. The maximum temperature at 1 cm below the surface was 191°C, which is really close to the 200°C expected for the decomposition of energetics. The temperature was lower for deeper thermocouples: 92, 65 and 62°C at 2, 5 and 8 cm, respectively. Nevertheless, this procedure of mixing sand with fuel seems promising for energetics remediation.

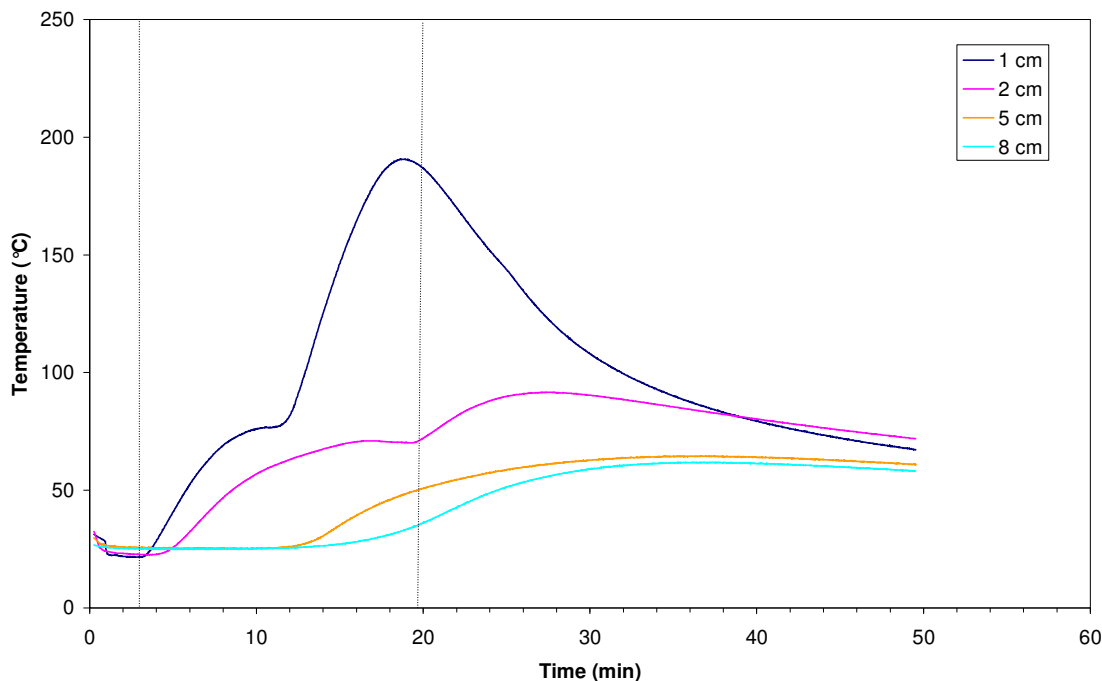


Figure 19 : Temperatures at different depths during the combustion of 500 mL of gelled ethanol mixed with 300 mL of sand (first cm of soil)

#### 4.2.7 Home-made ethanol gel

As the commercial ethanol gel used for the first tests contained water in an unknown amount, we tried to make our own home-made gel with a small proportion of water. A quick synthesis of gelled ethanol using calcium acetate was thus carried out. The protocol was inspired from a high-school chemistry laboratory [17]. Calcium acetate was dissolved in water, and then ethanol was added by increments, thus forming instantaneously a gel. After each addition, the gel was mixed with an electric blender to ensure a good homogenisation. The proportions were 17 g of calcium acetate, 50 mL of water and 800 mL of ethanol. This gel is stable, but tends to harden after a couple of hours. A quick mix in the blender was enough to recover the original texture.

A volume of 500 mL of home-made gel was spread on the soil, giving approximately 1.25 cm thick. Two tests were carried out, both lasted for around 12 minutes. The readings of the thermocouples for one test are presented in Figure 20. The maximum temperature reached at 1 cm below the surface is around 52°C for the first test, and 65°C for the second. These temperatures were lower than the temperature reached with the same volume of commercial gelled ethanol (130°C).

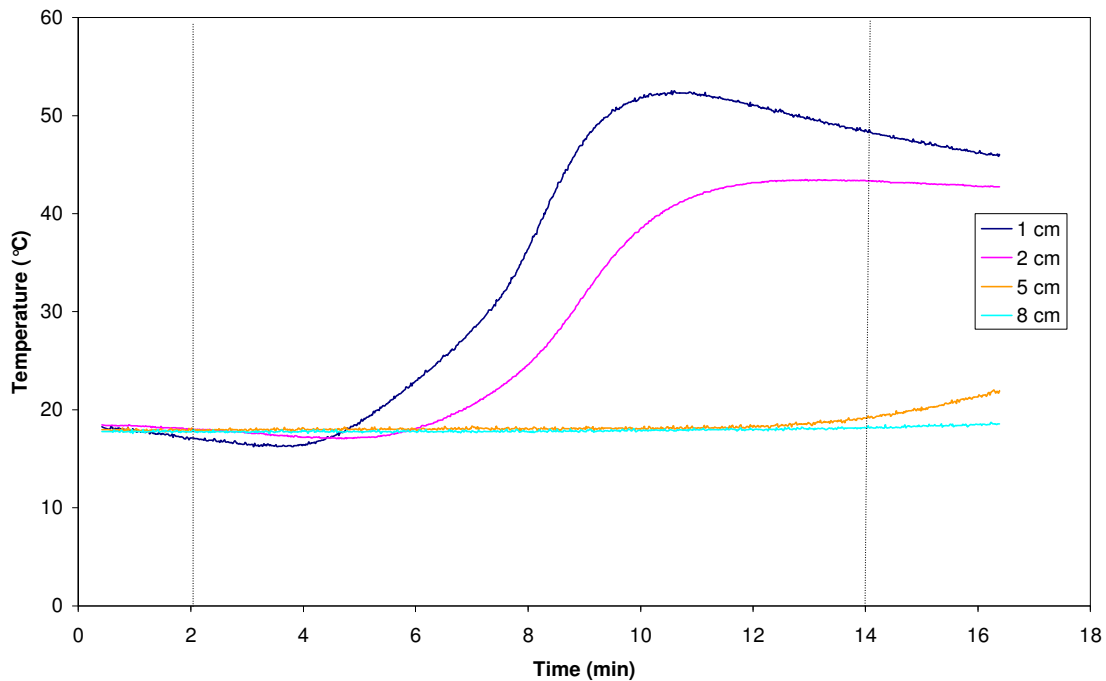


Figure 20 : Temperatures at different depths during the combustion of 1.25 cm thick of home-made ethanol gel (with calcium acetate)

#### 4.2.8 Sand/ethanol gel mix

The same setup as for the sand/gelled ethanol mix was used, but with the home-made ethanol gel. The first cm of sand (300 mL approximatively) was removed from the aluminium container and mixed in a separate vessel with 500 mL of home-made ethanol gel. This mixture was then returned in the container, so that the thermocouple at 1 cm below the surface was in contact with sand (below) and sand-gel mixture (above). The fire burned for about 19 minutes. The temperature at various depths is presented in Figure 21. The maximum temperature at 1 cm below the surface was 85°C. The temperature was lower for deeper thermocouples: 69, 47 and 28°C at 2, 5 and 8 cm, respectively. The temperatures are much lower than the ones obtained when burning the commercial gelled ethanol. A technical problem caused the end of the recording for the 5-cm deep probe before the end of the burning. Unfortunately, the recording was stopped right at the end of the burning. The observations were that the temperature began to decrease at the end of the burning, as it was observed for the gelled ethanol mixed with sand (Figure 19).

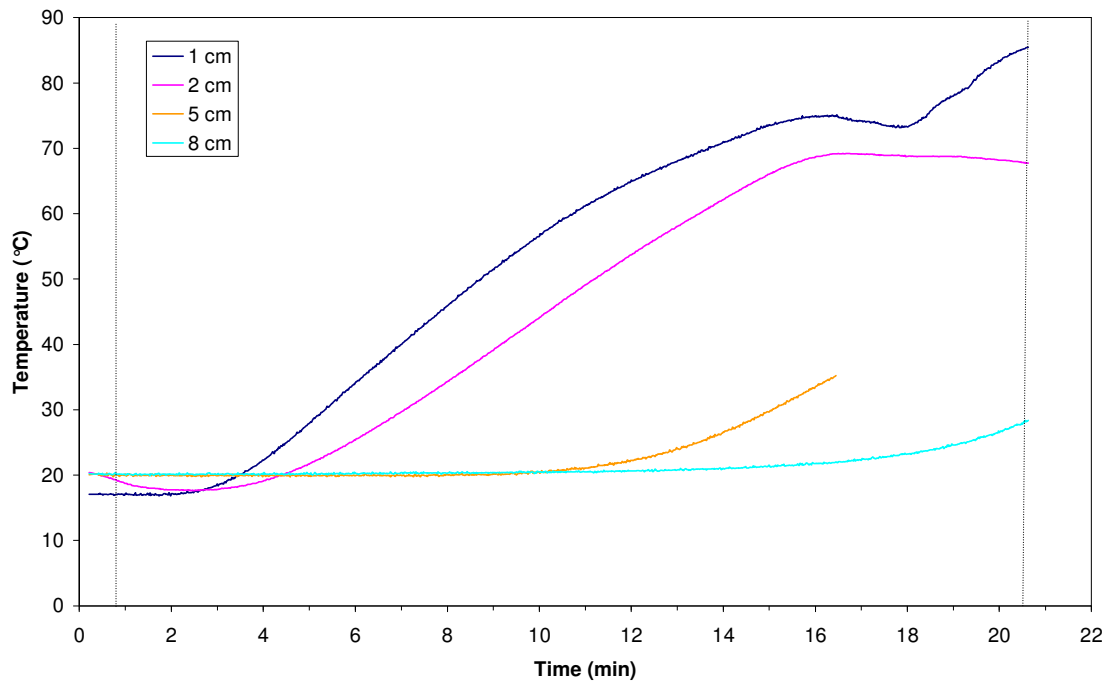
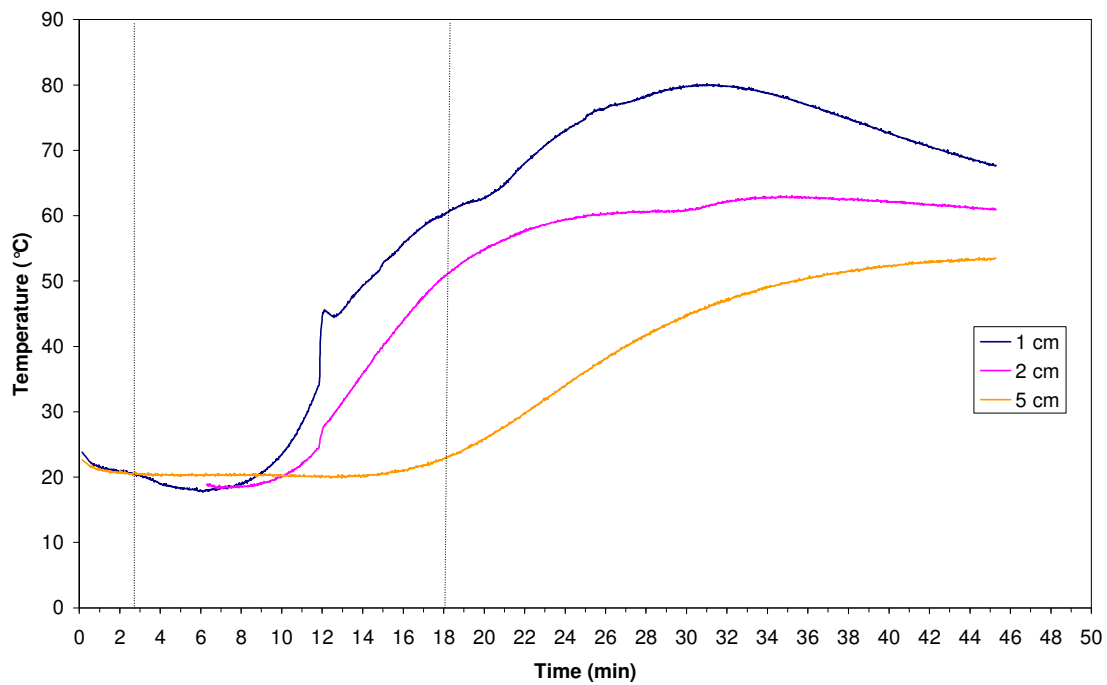


Figure 21 : Temperatures at different depths during the combustion of 500 mL of home-made ethanol gel mixed with 300 mL of sand (first cm of soil)

#### 4.2.9 Ethanol gel with activated carbon

The home-made gel was mixed with activated carbon to determine if this mixture could increase the burning temperature. The results for a mixture of 50 mL of activated carbon and 500 mL of home-made gel (approximately 1.25 cm thick) are presented in Figure 22. The burning lasted for around 15 minutes. As opposed to the other burnings, the temperature in the soil continued to increase after the end of the burning itself. The maximum temperature attained at 1 cm below the surface was 80°C. This is a little over the maximum temperature obtained with the gel only.



*Figure 22 : Temperatures at different depths during the combustion of 500 mL of home-made ethanol gel mixed with 50 mL of activated carbon (1.25 cm thick)*

A summary of the results obtained with the different fuels tested is presented in Table 3. The maximum temperature obtained at each thermocouple is shown in the table.

*Table 3 : Summary of the maximum temperature reached during the burning of various fuels on sand*

Fuel	Maximum temperature at various depths (°C)			
	1 cm	2 cm	5 cm	8 cm
Gelled ethanol (1.25 cm thick)	131	63	50	49
Gelled ethanol (1.25 cm thick) (duplicate)	106	72	52	51
Gelled ethanol (2.5 cm thick)	80	68	61	57
Gelled methanol (1 cm thick)	90	57	53	53
Wood shavings (3.8 cm thick)	25	22	22	22
Wood shavings (3.8 cm thick) soaked with ethanol	80	57	54	52
Ethanol (500 mL)	63	50	38	36
Isopropyl alcohol (500 mL)	33	29	27	33
Methanol (500 mL)	28	28	27	33
1 <sup>st</sup> cm of sand mixed with gelled ethanol (~ 1:1 v/v)	191	92	65	62
Home-made ethanol gel (with calcium acetate) (1.25 cm thick)	65	58	31	21
Home-made ethanol gel (with calcium acetate) (1.25 cm thick) (duplicate)	53	43	22	20
1 <sup>st</sup> cm of sand mixed with home-made ethanol gel (with calcium acetate) (~ 1:1 v/v)	85	69	48	28
Activated carbon (50 mL) mixed with home-made gel (500 mL)	80	63	54	----

The use of a propane torch, even though it seemed to be promising after Phase 1, was removed from the list because it may be difficult to implement as a remediation technique on a large-scale field area because it would be difficult to ignite remotely. The most promising fuel is the commercial gelled ethanol. It will be used for Phase 3 tests.



## **5 Phase 3 : Determination of the efficiency of destruction of residual energetic materials in contaminated soils by controlled burns**

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The aim of this part of the work was to evaluate the efficiency of destruction of residuals energetic compounds in contaminated soil taken in a real training area. The most promising combustible materials as determined during Phase 2 were ignited on the top of a certain volume of soil and nitroglycerine concentration was monitored before and after the burning. These tests were carried out in January 2009.

### **5.1 Experimental method**

#### **5.1.1 Contaminated soil**

The soil used for the tests of Phase 3 came from the firing position of Liri Range, an active anti-tank firing range which is known to be contaminated with energetic materials. Liri Range is situated within the Canadian Forces Base Valcartier, near Québec City. The soil was taken in autumn 2008 and dried at room temperature in the dark. The soil was kept in closed plastic pails until needed for trials.

#### **5.1.2 Burning**

Before the burning procedure, the soil was placed in a container and the fuel was spread over it. It was ignited with the same procedure as in Phase 2. Some tests were carried out in the cubic aluminium container (same as used in Phase 2), and some other were carried in a pyrex vessel (same as used in Phase 1). The main difference is that the air supply may be better when using the pyrex plate since the soil is closer to the top of the walls. The ignition of the fuel was made using the same technique as in Phase 2 (see subsection 4.1.3). Pictures of a burning of gelled ethanol is shown in Figure 23.



*Figure 23 : Burning of gelled ethanol over contaminated soil : a) gel spread on the soil (left plate gel on top, right plate gel mixed with first cm of soil); b) side view, c) burning; d) soil after combustion*

### 5.1.3 Sampling and analysis for energetic materials

The soil used for Phase 3 was contaminated with energetic materials. In order to determine if the combustion had any effect on the concentration of energetic contaminants, samples were taken before and after the burning procedure. A metal spatula was used to build different samples, each of total mass between 10 and 40 g and composed of 15 increments. One sample was taken on the surface (0 to 1 cm depth), and one at 2 cm deep for each fuel tested, thus giving a total of 12 samples to analyze. As the samples were composed of soil that had been previously sieved, they were not sieved again before analysis. Also, as the samples were small, they were not homogenized with acetone as done with large samples usually taken for soil characterization studies [18]. They were directly and completely mixed with acetonitrile in proportion of 2 mL of solvent for 1 g of soil in a glass jar. The jars were shaken with a vortex shaker for 1 minute, followed by sonication in a cooled ultrasonic bath for 18 hours. The solutions were then let to settle for 30 minutes before the preparation of the sample for analysis. Dilutions were made when

necessary, making sure that the final solution for injection in the HPLC apparatus was a mix 1:1 v/v acetonitrile and water. The solution was filtered with a 0.45- $\mu$ m filter and analyzed by HPLC using an in-house method derived from current EPA analysis methods (US EPA SW846 method 8330b), previously described in subsection 3.1.3.

## 5.2 Results

As presented in subsection 5.1.3, sampling was done on the surface of the contaminated soil (0-1 cm depth) and at 2 cm deep. The results of the burning for the surface soil are presented in Table 4. The concentration of NG showed a reduction for most of the thermal treatments. Some treatments, such as burning gelled methanol over the soil and propane burning were not efficient in reducing the NG concentration. The temperature did not increase enough or for a sufficient duration. Propane burning was quite efficient with a small amount of soil (Phase 1, Section 3.2) with a 80 % reduction of NG concentration, but it is not efficient in medium-scale conditions.

The commercial gelled ethanol offered the most interesting result. When placed directly over the soil, the combustion of gelled ethanol gave a decrease of 76 and 53 % in NG concentration (two different trials). When the gel was mixed with the first layer of soil, the reduction for NG was over 90 % (two trials). Future trial should include the analysis of more samples taken before and after burning to determine the error associated with the reduction percentage. At this moment, these values should only be considered as indicators that the best method is the burning with commercial gelled ethanol.

*Table 4 : Results for NG in surface (0-1 cm deep) soil samples for various burning configurations*

<b>Thermal process</b>	<b>[NG] (mg/kg) before</b>	<b>[NG] (mg/kg) after</b>	<b>Reduction (%)</b>
500 mL gelled ethanol (commercial)	2365	557	76
Mix 500 mL gelled ethanol (commercial) + 300 mL contaminated soil	2548	152	94
500 mL gelled ethanol (commercial) *	2537	1190	53
500 mL gelled ethanol (commercial) + 500 mL soil *	2947	235	92
5 min of propane burning *	2480	1547	38
400 g methanol gel	2075	1847	11

\* : burning carried out in a Pyrex plate.

## 6 Conclusion and future work

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Experimental results confirmed that much of the heat produced during the combustion of various fuels is directed upwards and that sands acts as an isolation barrier, preventing the destruction of EMs in the deeper layers of soil. The use of a thicker layer of combustible did not increase the temperature as the unburned fuel acted as an isolating barrier. From the test carried out, the most promising fuel was a commercial gelled ethanol (Gelled fuel, Home Presence by Trudeau, Montreal, QC). When mixing the first cm of soil with the gel in a 1:1 v/v proportion, a temperature of  $> 190^{\circ}\text{C}$  at 1cm below the soil surface was reached.

Contaminated soil taken from the firing position of an anti-tank firing range was monitored for nitroglycerine concentration, before and after the combustion of selected fuels. Soils samples were extracted using acetonitrile and NG was analyzed by HPLC. The concentration of NG showed a reduction for most of the thermal treatments tested, but only in the surface soils (0-1 cm). The commercial gelled ethanol offered the most interesting results, with a decrease of 76 and 53 % when placed directly over soil for two separated trials. The best performances were obtained with the same ethanol gel, but when the gel was mixed with the first layer of soil. In these conditions, the reduction for NG was over 90 % for the two trials.

The next step would be to use the most promising fuel, i.e. the commercial gelled ethanol directly on a range in real conditions, such as soil humidity, inhomogeneous soil, winds, etc. to determine if this controlled burning is a viable alternative for soil decontamination that may be used on a large scale. In laboratory conditions, when the gel was mixed with the first layer (0-1 cm) of soil, the reduction in nitroglycerine concentration was over 90 %. This trial has been carried out in Autumn 2009 at CFB Gagetown and will be the subject of a future report (Phase 4).

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## Annex A FT-IR spectra of dried ethanol/water gel

The commercial ethanol/water was dried and the residue analyzed by Fourier-transformed infrared (FT-IR) spectrometry to determine its composition. The system is an Excalibur model FTS-3000 equipped with a microscope model UMA 600 from Varian. The spectrum was taken on a slide-on attenuated total reflection (ATR) accessory with a germanium crystal.

The best match with the spectrum of the residue is hydroxypropylmethyl cellulose. This product is most probably the thickening agent for the gel. The spectra of the residue and hydroxypropylmethyl cellulose (from the library) are shown in Figure A-1.

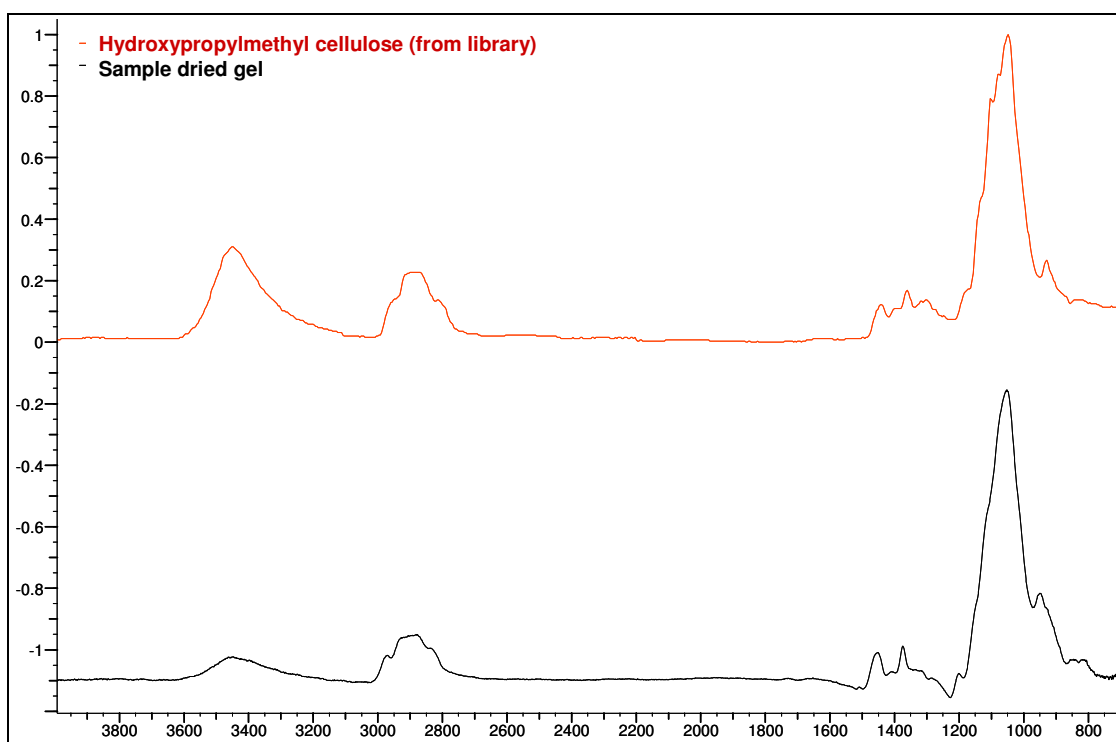


Figure A-1: FT-IR spectrum of dried ethanol/water gel and hydroxypropylmethyl cellulose

FTIR conditions : Region : 400-4000  $\text{cm}^{-1}$

Aperture : 1

Filter : 5

Sensitivity : 1.5

Resolution : 2  $\text{cm}^{-1}$

Speed : 20 KHz

Detector : MCT

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## List of symbols/abbreviations/acronyms/initialisms

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ACN	acetonitrile
ASU	Air Support Unit
CFB	Canadian Forces Base
DNB	Dinitrobenzene
DND	Department of National Defence
DNT	Dinitrotoluene
DOD	Department of Defence (USA)
DRDC	Defence Research & Development Canada
DRDKIM	Director Research and Development Knowledge and Information Management
EM	Energetic materials
h	Hour
HMX	Octogen, or cyclotetrametylenetetranitramine
HPLC	High Performance Liquid Chromatography
min	Minute
mL	Milliliter
mm	Millimeter
MMR	Massachusetts Military Reservation
NG	Nitroglycerine
nm	Nanometer
PAH	Polycyclic aromatic hydrocarbon
PCP	Pentachlorophenol
ppm	Part per million (mg/kg)
R&D	Research & Development
RDX	Hexogen, or cyclo-1,3,5-trimethylene-2,4,6-trinitramine
TNT	Trinitrotoluene
US DOD	United States Department of Defense
USAEC	United States Army Environmental Center
USEPA	United States Environmental Protection Agency

UV	Ultraviolet
UXO	Unexploded ordnance
µm	Micron

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As a result of military training, many ranges and training areas are contaminated with energetic materials (EMs). In Canada, for many sites characterized, more than 80 % of the overall contamination by EMs was found in the first 10 cm of the surface soil for propellant residues at the firing positions. Military personnel can be exposed to these compounds which may eventually be transported to surface and groundwater. At this moment, there is no official protocol for routinely removing propellant residues from surface soils. Various remediation strategies are currently being studied (phytoremediation, fire ecology, etc.) in order to address the problem of surface soils contamination by EMs. This report presents the work carried out to evaluate up to which extent the combustion of selected fuels (liquids and gels) could be used as a remediation method for the thermal decomposition of propellants in surface soils. In Phase 1, preliminary tests were carried out to quickly evaluate the potential of fuel combustion over soil as a remediation procedure. In Phase 2, temperature propagation in sand was determined during burnings. In Phase 3, contaminated soil taken from the firing position of an anti-tank range was monitored for nitroglycerine before and after the combustion of a top layer of selected fuels. The results showed that a gelled ethanol fuel is promising for the remediation of contaminated soils by energetic materials

En raison des exercices d'entraînement militaire, plusieurs sites sont contaminés par des matériaux énergétiques. Au Canada, dans plusieurs pas de tir contaminés par les résidus de poudres propulsives, plus de 80 % de la contamination totale se trouve dans les premiers 10 cm de sol. Le personnel militaire peut être exposé à ces composés qui peuvent aussi être transportés dans l'eau de surface et souterraine. Actuellement, il n'y a pas de protocole officiel pour retirer périodiquement les résidus de poudres propulsives des sols de surface. Plusieurs stratégies de restauration sont présentement à l'étude (phytoremédiation, écologie du feu, etc.) dans le but d'examiner le problème de la contamination des sols de surface par les matériaux énergétiques. Ce rapport présente les travaux réalisés pour évaluer à quel point la combustion de carburants (liquides et gels) pourrait être utilisée comme méthode de restauration pour effectuer la décomposition thermique des résidus de poudres propulsives dans les sols de surface. Durant la Phase 1, des tests préliminaires ont été réalisés pour évaluer rapidement le potentiel du brûlage d'un carburant sur un sol contaminé comme procédure de restauration. Durant la Phase 2, des mesures de propagation de la température dans le sable ont été prises durant des brûlages. Durant la Phase 3, du sol contaminé pris sur un pas de tir d'un site anti-char a été analysé pour mesurer la nitroglycérine avant et après la combustion d'une couche de combustibles sélectionnés. Les résultats montrent qu'un gel à base d'éthanol est très prometteur pour la restauration des sols contaminés par les matériaux énergétiques.

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Soil; contamination; energetic materials; nitroglycerine; Canadian Forces Base; ranges; training area; combustion; remediation; fuel; ethanol; heat propagation



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